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(54) Title: LEAVE-ON HAIR COMPOSITIONS WHICH CONTAIN A DIOL (57) Abstract The present invention relates to a leave-on hair care composition comprising from about 3 % to 30 %, by weight, of a diol selected from the group consisting of 1,2 C ₅ -C ₈ -alkane diols, C ₂ -C ₁₀ -alkyl glyceryl ethers, and mixtures thereof; from about 70 % to about 97 %, by weight, of a polar solvent selected from the group consisting of water, C ₂ -C ₃ monohydric alkanols, and mixtures thereof; and from about 0.015 to about 20 %, by weight, of a hair care ingredient.		

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LEAVE-ON HAIR COMPOSITIONS WHICH CONTAIN A DIOL

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims the benefit under 35 USC §119(e) of the U.S. provisional application of Daniel Wayne Michael and Errol Hoffman Wahl having Serial No. 60/091,016, filed June 29, 1998; and the U.S. provisional application of Daniel Wayne Michael and Errol Hoffman Wahl having Serial No. 60/110,435, filed December 1, 1998.

TECHNICAL FIELD

The present invention relates to leave-on hair care compositions which provide improved hair conditioning properties. These compositions comprise a diol selected from either 1,2 C₅-C₈-alkane diols or C₂-C₁₀-alkyl glyceryl ethers. These products deliver unexpected reduction of hair frizziness without leaving an oily feel to the hair. The leave-on hair-care products are easy to remove, and therefore do not build up on the hair with repeated use. The compositions are used in leave-on products such as hair tonics, hair sprays, gels, mousses, and the like.

BACKGROUND OF THE INVENTION

Scalp hair becomes soiled due to its contact with the surrounding environment and from sebum secreted from the hair follicles. The build-up of sebum and environmental soiling can cause the hair to have a dirty or greasy feel, and an unattractive appearance. In order to ameliorate these effects, it is necessary to shampoo the hair with regularity.

Shampooing the hair removes excess sebum and other environmental soiling, but has the disadvantage of leaving the hair in a wet, tangled, and relatively unmanageable state. Frequent shampooing can also result in the hair becoming dry due to the removal of natural oils or other hair moisturizing materials. After shampooing, the hair can also suffer from a perceived loss of "softness." Frequent shampooing also contributes to the phenomena of "split ends," particularly for long hair. Split ends refers to a condition wherein the ends of the hair are split into two or more shafts, resulting in a frizzy appearance.

Also, many people have hair which by its curly nature has a high volume or frizzy appearance. Many people regularly perm and/or color their hair. It is known that these types of treatments generally can dry out, and even damage the hair. This damaged hair is less soft and will have a frizzy appearance. Often, people whose hair has a frizzy appearance wish to reduce the volume of their hair thereby reducing the frizzy look. Traditionally, people have used a general hair conditioner to help reduce frizz.

A variety of approaches have been developed to condition the hair. These range from post-shampooing hair rinses, to leave-on hair conditioner tonics and sprays, to the inclusion of hair conditioning components in shampoos. Although many consumers prefer the ease and convenience of a shampoo which includes conditioners, typical shampoo-and-conditioner combinations alone do not provide sufficient conditioning to reduce the frizzy appearance from damaged hair, hair with split ends, or naturally curly hair.

Also, a substantial proportion of consumers prefer using the conditioner formulations which are applied to the hair as a separate step from shampooing, usually subsequent to shampooing. These hair conditioners are typically either rinse-off conditioners, used immediately after shampooing in the shower, bath or sink, or leave-on conditioning products, used separately from the shampooing step. Rinse-off conditioners typically contain silicone conditioning agents or quaternary ammonium compounds which deposit on the hair. These conditioners are generally applied to wet hair immediately after shampooing and then rinsed from the hair. However, typical rinse-off conditioners also do not provide sufficient frizz reduction to benefit people with frizzy hair.

Leave-on conditioners are sold as gels, tonics, sprays or mousses depending on the mode chosen for dispensing the product for application to the hair. These leave-on conditioners also generally contain silicone conditioning agents or quaternary ammonium compounds. These leave-on conditioners generally provide high levels of the conditioning compounds. However, while the leave-on conditioners result in frizz reduction, the high level of deposited quaternary compounds and/or silicones result in hair feeling slick, oily and dirty. Also, typical leave-on conditioners build up with use, even with regular shampooing of the hair. This build-up accentuates the oily, dirty hair feel characteristics of typical products.

Polyols have been widely used in hair care compositions as humectants and moisturizers. Polyols, including 1,2 hexanediol, have been studied for their impact on hair damage and hair flexibility by Hosokawa et al. in "The Effects of Polyols on Human Hair", J. Soc. Cosmet. Chem. Jpn., 31(2), 167 -175 (1997). Hosokawa teaches polyols, such as glycerin, hexylene glycol, and 3-methyl-1,3-butanediol, as having the effect of making hair more flexible. Hosokawa also teaches that polyols having long carbon chain lengths (e.g. 1,2 hexanediol) have higher permeability of hair.

It has been found, in the present invention, that leave-on hair care compositions containing 1,2 C₅-C₈-alkane diols or C₂-C₁₀-alkyl glyceryl ethers provide both conditioning sufficient to reduce the frizzy appearance from damaged, split end, or naturally curly hair, and a clean feel. It is an object of this invention to provide hair care compositions for application to the hair, which are not rinsed off after use, which provide this combination of conditioning and clean feel.

It is also an objective of the present invention to provide a method for conditioning hair to reduce frizzy appearance with the above compositions.

These and other objects and benefits of the present invention as may be set forth herein as may now or later become apparent to those skilled in the art can be provided according to the invention which is described herein.

The invention hereof can comprise, consist of, or consist essentially of the essential elements, described herein as well as any of the preferred or other optional ingredients described herein.

All percentages herein are by weight of the total composition unless otherwise indicated. All ratios are weight ratios unless otherwise indicated. Unless otherwise indicated, all percentages, ratios, and levels of ingredients referred to herein are based on the actual amount of the ingredient, and do not include solvents, fillers, or other materials with which the ingredient may be combined in commercially available products. All measurements are at 25°C or room temperature, unless otherwise designated.

All documents referred to herein, including all patents, all patent applications, all articles, all bulletins, all pamphlets, and all technical data sheets are incorporated herein by reference in their entirety.

SUMMARY OF THE INVENTION

The present invention relates to leave-on hair care compositions comprising from about 3% to 30%, by weight, of a C₂-C₁₀-alkyl glyceryl ether; and from about 70% to about 97%, by weight, of a polar solvent selected from the group consisting of water, C₂-C₃ monohydric alkanols, and mixtures thereof. The invention also relates to leave-on hair care compositions comprising from about 3% to 30%, by weight, of a 1,2 C₅-C₈-alkane diols; and from about 70% to about 97%, by weight, of a polar solvent selected from the group consisting of leave-on vehicle comprising a hair care ingredient selected from the group consisting of C₂-C₃ monohydric alkanols and mixtures of C₂-C₃ monohydric alkanols and water.

Further embodiments of these inventions relate to leave-on hair care compositions comprising from about 3% to 30%, by weight, of a diol selected from the group consisting of 1,2 C₅-C₈-alkane diols, C₂-C₁₀-alkyl glyceryl ethers, and mixtures thereof; from about 70% to about 97%, by weight, of a polar solvent selected from the group consisting of water, C₂-C₃ monohydric alkanols, and mixtures thereof; and from about 0.015 to about 20%, by weight, of a hair care ingredient selected from the group comprising conditioning agents, nonionic surfactants, thickeners, perfumes, preservatives, pH adjusting agents, coloring agents, propellants, vitamins and derivatives thereof, vitamin penetration aids, hair spray spray modifiers, and mixtures thereof; wherein the hair care composition comprises less than about 0.1% of hair reducing agents..

DETAILED DESCRIPTION OF THE INVENTION

The term "leave-on", as expressed herein to modify the term "hair care composition", is used to indicate that the compositions of the present invention are intended to be applied to and allowed to remain on the hair. These leave-on compositions are to be distinguished from "rinse-off" compositions which are applied to the hair and subsequently removed, either immediately or after a few minutes, either by washing, rinsing, wiping or the like. In order to achieve the hair conditioning benefits, the composition of the present invention must remain on the hair at least until the hair is dry.

The leave-on compositions of the present invention may be of any product form which is applied to the hair and not rinsed off. Product forms may be selected from the group consisting of gels, tonics, lotions, mousses, and sprays.

The essential ingredients as well as a non-inclusive list of preferred and optional ingredients are described below.

Diol

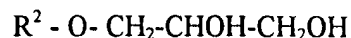
The compositions of the present invention comprise from about 3% to about 30%, preferably from about 4% to about 25%, more preferably from about 5% to about 20%, and most preferably from about 7% to about 15% of a diol. The diol may be a 1, 2 C₅-C₈-alkane diol, a C₂-C₁₀-alkyl glyceryl ether, or a mixture thereof.

The 1,2 C₅-C₈-alkane diols are compounds of the formula:



where R¹ is an propyl, butyl, pentyl, or hexyl group. R¹ may be straight chain or branched groups, preferably straight chain. The preferred alkane diols are 1,2 n-pentane diol, 1,2 n-hexane diol, 1,2 n-heptane diol, or mixtures thereof. Most preferred is 1,2 n-hexane diol, where R¹ is n-butyl.

The C₂C₁₀-alkyl glyceryl ethers are compounds of the formula:



where R² is an ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, or decyl group. R² may be straight chain or branched groups, preferably straight chain. The preferred glyceryl ethers are n-propyl-, n-butyl-, n-pentyl-, n-hexyl glycerol ethers and mixtures thereof. Most preferred is n-hexyl glyceryl ether.

Polar Solvent

The leave-on hair care compositions of the present invention also comprise a polar solvent as a liquid vehicle for the diol. A polar solvent is any solvent material with a dielectric constant at 25°C greater than about 5.0, preferably greater than about 7.5 and more preferably greater than about 10.0. The polar solvent of the present invention comprises one or more polar solvents that are present in the hair care compositions at a level

of from about 70% to about 97%, preferably from about 80% to about 95%, more preferably from about 85% to about 93% of the total composition.

The polar solvents essential to the present compositions are selected from the group consisting of water, C₂-C₃ monohydric alkanols, and mixtures thereof. If present, C₃ alkanols, such as isopropanol, should be used at levels no greater than about 15% by weight of the composition, preferably no greater than about 12%, more preferably no greater than about 10%. High levels of C₃ monohydric alcohols are undesirable in the present compositions due to potential odor issues they can create. Preferred polar solvent phases contain water, ethanol, or mixtures thereof.

Where water and alcohol mixtures are used, for instance, water-ethanol or water-isopropanol-ethanol, the water content of the compositions is generally in the range of from about 0.5% to about 99%, by weight of the total composition. In such mixtures, the alcohol solvents are generally present in the range of from 0.5% to about 99%, by weight of the total composition.

Hair Care Ingredient

The compositions of the present invention can comprise a wide range of additional hair care ingredients suitable for rendering such compositions more cosmetically or aesthetically acceptable or to provide them with additional usage benefits. The CTFA Cosmetic Ingredient Handbook, Second Edition, 1992, which is incorporated by reference herein in its entirety, describes a wide variety of nonlimiting cosmetic ingredients commonly used in the hair care industry. These additional ingredients include: other conditioning agents; surfactants, such as anionic, nonionic, amphoteric, and zwitterionic surfactants; thickeners, such as xanthan gum, guar gum, hydroxyethyl cellulose, methyl cellulose, hydroxyethylcellulose, starch and starch derivatives, Carbomers®; perfumes; preservatives; polymers; pH adjusting agents; coloring agents, such as any of the FD&C or D&C dyes; polymer plasticizing agents, such as glycerin, disobutyl adipate, butyl stearate, and propylene glycol; propellants; vitamins and derivatives thereof, such as panthenol and other derivatives of pantothenic acid, pantothenic ethers; vitamin penetration aids, such as polyethylene glycol or polypropylene glycol having from 3 to about 12 ethylene glycol or propylene glycol units, hair spray spray modifiers, such as polyethylene glycol having from about 2000 to about 25,000 ethylene glycol units. Such optional ingredients generally are used individually at levels from about 0.01% to about 20.0%, preferably from about 0.05% to about 15.0%, more preferably from about 0.1% to about 10%, even more preferably from about 0.5% to about 8%, most preferably from about 1% to about 5% of the composition. Detailed descriptions of preferred hair care ingredients follow.

Perfume / Preservative

Preferred leave-on hair care compositions comprise a perfume and a preservative. Perfumes are well known in the art to deliver aesthetically pleasing aroma to the hair in addition to reduced frizz and clean feel of the diol of the present invention. Perfumes are used in the compositions of the present invention at levels of from about 0.01% to about 4%, preferably from about 0.05% to about 2.5%.

Non-limiting examples of preservatives which may be used in the leave-on composition of the present invention are benzyl alcohol, methyl paraben, propyl paraben, DMDM hydantoin, methylchloroisothiazoline, methylisothiazolinone, and imidazolidinyl urea. Preservatives are used in the compositions of the present invention at levels of from about 0.001% to about 1%.

Anionic Surfactant

Preferred compositions of the present invention may contain low levels anionic surfactant. The anionic surfactant may be present at levels of from about 0.01% to about 2%, preferably from about 0.05% to about 1%, and more preferably from about 0.1% to about 0.5%. Nonlimiting examples of anionic lathering surfactants useful in the compositions of the present invention are disclosed in McCutcheon's, Detergents and Emulsifiers, North American edition (1990), published by The Manufacturing Confectioner Publishing Co.; McCutcheon's, Functional Materials, North American Edition (1992); and U.S. Patent No. 3,929,678, to Laughlin et al., issued December 30, 1975, all of which are incorporated by reference.

A wide variety of anionic surfactants are potentially useful herein. Nonlimiting examples of anionic lathering surfactants include those selected from the group consisting of alkyl and alkyl ether sulfates, sulfated monoglycerides, sulfonated olefins, alkyl aryl sulfonates, primary or secondary alkane sulfonates, alkyl sulfosuccinates, acyl taurates, acyl isethionates, alkyl glycerylether sulfonate, sulfonated methyl esters, sulfonated fatty acids, alkyl phosphates, acyl glutamates, acyl sarcosinates, alkyl sulfoacetates, acylated peptides, alkyl ether carboxylates, acyl lactylates, and anionic fluorosurfactants. Mixtures of anionic surfactants can be used effectively in the present invention. Preferrable anionic surfactants are alkyl and alkyl ether sulfates. Ammonium and sodium lauryl sulfate are most preferred.

Nonionic Surfactant

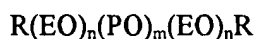
Preferred compositions of the present invention may contain a nonionic surfactant. The nonionic surfactants useful herein include any of the well-known nonionic surfactants that are liquid at room temperature, have an HLB of from about 4 to about 20 depending on the class of nonionic surfactant chosen.

The leave-on hair care compositions of the present invention can comprise from about 0.01% to about 20%, preferably from about 0.1% to about 5%, more preferably from about 0.5% to about 3%, of nonionic surfactant.

Two typical groups of nonionic surfactants are the alkoxyated (especially ethoxylated) alcohols and the alkyl pyrrolidones, and the like, which are well-known from the surfactant art. In general, such nonionic surfactants contain a C_{4-22} , preferably C_{6-16} , more preferably all C_{8-14} alkyl group. Also, preferred is nonionic surfactant containing a $C_{18:1}$ group, the oleyl alkenyl group. Ethoxylated surfactant generally contain from about 2 to about 12, preferably from about 2.5 to about 10, more preferably from about 3 to about 8, ethylene oxide groups, to give an HLB of from about 4 to about 10, preferably from about 5 to about 9, and more preferably from about 6 to about 8. Ethoxylated alcohols are especially preferred in the compositions of the present invention.

Specific examples of ethoxylated nonionic surfactants useful herein include: octyl polyethoxylates (2.5) and (5); decyl polyethoxylates (2.5) and (5); decyl polyethoxylate (6); dodecyl polyethoxylate (3), tridecyl polyethoxylate (3), coconut alkyl polyethoxylate (6.5), oleyl polyethoxylate (3), and mixtures thereof.

Also preferred in the present invention are nonionic surfactants which are block copolymers of propylene glycol and ethylene glycol. These nonionic surfactants have the formula:



wherein EO is ethylene oxide, PO is propylene oxide, each of n and m are selected to give a surfactant having a total molecular weight of from about 200 to about 8,000, and each R being selected from hydrogen (preferred) and hydrocarbon groups, preferably C_{1-4} hydrocarbon groups. These surfactants can have m and n vary to provide any EO content. Such surfactants typically have an HLB of from about 4 to about 10, preferably from about 5 to about 9, and more preferably from about 6 to about 8 as required heretofore.

A detailed listing of suitable nonionic surfactants, of the above types, for the leave-on hair care compositions herein can be found in U.S. Pat. No. 4,557,853, Collins, issued Dec. 10, 1985, incorporated by reference herein. Commercial sources of such surfactants can be found in McCutcheon's EMULSIFIERS AND DETERGENTS, North American Edition, 1984, McCutcheon Division, MC Publishing Company, also incorporated herein by reference.

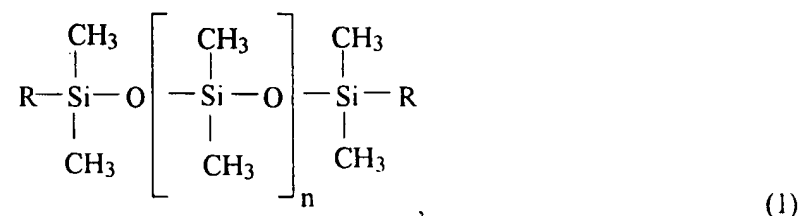
Preferable block copolymers of propylene glycol and ethylene glycol have a total molecular weight of from about 3,000 to about 10,000, preferably from about 4,000 to about 8,000, and each R being selected from hydrogen (preferred) and hydrocarbon groups, preferably C_{1-4} hydrocarbon groups. These preferable nonionic surfactants have an EO content of from about 20% to about 80%, preferably from about 20% to about 40%.

Another preferable block copolymers of propylene glycol and ethylene glycol have a total molecular weight of from about 200 to about 2,000, preferably from about 500 to about 1,000, and each R being hydrogen, and having an EO content of less than about 50%.

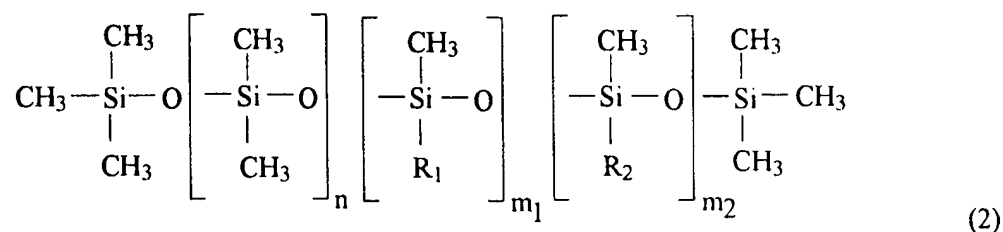
preferably less than about 10% and most preferably equal to 0%, i.e. 100% polypropylene glycol.

Also preferred in the present invention are nonionic silicone surfactants such as silicone copolyols, or polydimethyl siloxanes.

The polydimethyl siloxanes which may be used in the compositions of the present invention are disclosed in Grüning, B. and Koerner, G., "Silicone Surfactants", Tenside Surf. Det. 26 (1989) 5, 312-317, and Schaefer, D., "Silicone Surfactants", Tenside Surf. Det. 27 (1990) 3, 154-158, incorporated herein by reference. These silicone surfactants may have the formula:



or



wherein R and R₁ represent a hydrophilic modifying group and R₂ represents a lipophilic modifying group. Preferred silicone surfactants must comprise substantially more hydrophilic modifying groups than lipophilic modifying groups. n can range from about 5 to about 25, preferably from about 10 to about 20, m₁ can range from about 1 to about 10, preferably from about 3 to about 7, and m₂ can be 0, 1, or 2, preferably 0.

The hydrophilic modifying groups preferably have the formula:



wherein EO is ethylene oxide and PO is propylene oxide and x and y are selected to give the hydrophilic modifying group molecular weight of from about 300 to about 1000. Preferred silicone surfactants have an HLB from about 10 to about 20, preferably from about 15 to about 19 and a cloud point (1% in water) from about 10°C to about 100°C, preferably from about 50°C to about 90°C.

Preferred silicone surfactants have the formula represented in formula (2), wherein R₁ has the formula:



n ranges from 13 to 20, m₁ is 5, m₂ is 0, x and y vary such that the weight ratio of EO:PO ranges from about 75:25 to about 100:0 and the total molecular weight of the silicone

surfactant is from about 2,000 to about 10,000. Most preferred examples of these silicone surfactants are Abil® B8843 and Abil® B8851, manufactured by Goldschmidt Chemical Corporation.

Silicone Grafted Polymer

The leave-on hair care compositions of the present invention may also preferably contain a silicone graft copolymer. The silicone graft copolymer, when used, may comprise from about 0.1 to about 5%, preferably from about 0.25% to about 2%, more preferably from about 0.5% to about 1% of the silicone graft copolymer.

Such graft copolymers can be prepared by a number of methods known to those skilled in the art, including:

1. Incorporation of silicone macromonomers in free radical polymerization. Such silicone functional polymers include the silicone graft copolymers described, along with methods of making them, in U.S. Patent 5,658,557, Bolich et al., issued August 19, 1997, U.S. Patent 4,693,935, Mazurek, issued September 15, 1987, and U.S. Patent 4,728,571, Clemens et al., issued March 1, 1988, each incorporated herein by reference.
2. Incorporation of silicone macromonomer in atom transfer radical polymerization. A method of making these types of polymers is generally described in Beers et al, "The Use of 'Living' Radical Polymerization to Synthesize Graft Copolymers," Polymer Preprints, pp 571-572, March, 1996, incorporated herein by reference.
3. Incorporation of vinyl polymeric grafts onto a silicone backbone by chain transfer to a pendant sulfhydryl group. Such sulfur linked silicone copolymers are described in detail in U.S. Patent No. 5,468,477, to Kumar et al., issued November 21, 1995, and PCT Application No. WO 95/03776, assigned to 3M, published February 9, 1995, which are incorporated by reference herein in their entirety. Additional patents with sulfur linked structures include U.S. 5,032,460, to Kanter et al, issued July 16, 1991, assigned to 3M and U.S. 5,362,485, to Hayama et al, issued Nov. 8, 1994, assigned to Mitsubishi Chem. Co.

The silicone grafted polymers are characterized by polysiloxane moieties covalently bonded to and pendant from a polymeric carbon-based backbone. The backbone will preferably be a carbon chain derived from polymerization of ethylenically unsaturated monomers, but can also be, cellulosic chains or other carbohydrate-derived polymeric chains to which polysiloxane moieties are pendant. The backbone can also include ether groups, i.e., C-O-C. The polysiloxane moieties can be substituted on the polymer or can be made by co-polymerization of polysiloxane-containing polymerizable monomers (e.g. ethylenically unsaturated monomers, ethers, and/or epoxides) with non-polysiloxane-containing polymerizable monomers.

The polysiloxane-grafted polymer should have a weight average molecular weight of at least about 20,000. There is no upper limit for molecular weight except that which limits applicability of the invention for practical reasons, such as processing, aesthetic characteristics, formulateability, etc. In general, the weight average molecular weight will be less than about 10,000,000, more generally less than about 5,000,000, and typically less than about 3,000,000. Preferably, the weight average molecular weight will be between about 50,000 and about 2,000,000, more preferably between about 75,000 and about 1,000,000, most preferably between about 100,000 and about 750,000.

Preferably, the grafted-polymers hereof when dried to form a film have a Tg or Tm of at least about -20°C, preferably at least about 20°C, so that they are not unduly sticky, or "tacky" to the touch. As used herein, the abbreviation "Tg" refers to the glass transition temperature of the non-polysiloxane backbone of the polymer, and the abbreviation "Tm" refers to the crystalline melting point of the non-siloxane backbone, if such a transition exists for a given polymer. Preferably, both the Tg and the Tm, if any, are above about -20°C, more preferably above about 20°C.

The silicone grafted polymers which may be used in the compositions of the present invention include "silicone-containing" (or "polysiloxane-containing") monomers, which form the silicone macromer pendant from the backbone, and non-silicone-containing monomers, which form the organic backbone of the polymer.

The preferred silicone grafted polymers comprise an organic backbone preferably a carbon backbone derived from ethylenically unsaturated monomers, such as a vinyl polymeric backbone, and a polysiloxane macromer (especially preferred are polydialkylsiloxane, most preferably polydimethylsiloxane) grafted to the backbone. The polysiloxane macromer should have a weight average molecular weight of at least about 500, preferably from about 1,000 to about 100,000, more preferably from about 2,000 to about 50,000, most preferably about 5,000 to about 20,000. Organic backbones contemplated include those that are derived from polymerizable, ethylenically unsaturated monomers, including vinyl monomers, and other condensation monomers (e.g., those that polymerize to form polyamides and polyesters), ring-opening monomers (e.g., ethyl oxazoline and caprolactone), etc. Also contemplated are backbones based on cellulosic chains, ether-containing backbones, etc.

Examples of useful polymers and how they are made are described in detail in U.S. Patent 4,693,935, Mazurek, issued September 15, 1987, and U.S. Patent 4,728,571, Clemens et al., issued March 1, 1988, both of which are incorporated herein by reference.

Suitable silicone grafted polymers are also disclosed in EPO Application 90307528.1, published as EPO Application 0 408 311 A2 on January 11, 1991, Hayama, et al., U.S. Patent 5,061,481, issued October 29, 1991, Suzuki et al., U.S. Patent 5,106,609, Bolich et al., issued April 21, 1992, U.S. Patent 5,100,658, Bolich et al., issued March 31,

1992, U.S. Patent 5,100,657, Ansher-Jackson, et al., issued March 31, 1992, U.S. Patent 5,104,646, Bolich et al., issued April 14, 1992, U.S. Serial No. 07/758,319, Bolich et al, filed August 27, 1991, and U.S. Serial No. 07/758,320, Torgerson et al., filed August 27, 1991, all of which are incorporated by reference herein.

The preferred silicone grafted polymers are comprised of monomer units derived from: at least one free radically polymerizable ethylenically unsaturated monomer or monomers and at least one free radically polymerizable polysiloxane-containing ethylenically unsaturated monomer or monomers.

The silicone grafted polymers hereof generally comprise from about 1% to about 50%, by weight, of polysiloxane-containing monomer units, i.e., monomer units polysiloxane-containing monomers (referred to herein as "C" monomers), and from about 50% to about 99% by weight, of non-polysiloxane-containing monomers.

The non-polysiloxane-containing monomer units can be derived from polar, or hydrophilic, monomers, "A" monomers, or mixtures of polar hydrophilic monomers and low polarity, or hydrophobic, "B" monomers.

Hydrophobic monomers means monomers which form substantially water insoluble homopolymers. Hydrophilic monomers means monomers which do not form substantially water insoluble homopolymers. Substantially water soluble shall refer to monomers that form homopolymers that are soluble in distilled (or equivalent) water, at 25°C, at a concentration of 0.2% by weight, and are preferably soluble at 1.0% by weight. Substantially water insoluble shall refer to monomers that form homopolymers that are not soluble in distilled (or equivalent) water, at 25°C, at a concentration of 0.2% by weight, and preferably not soluble at 0.1% by weight. The weight average molecular weight for purposes of determining substantial water solubility or insolubility shall be about 100,000, although solubility at higher molecular weight shall also be indicative of solubility at about 100,000.

The particular relative amounts of A, B, and C monomers can vary as long as the polymer backbone is soluble in the polar solvent hereof and the silicone grafted copolymer exhibits phase separation when dried.

Representative examples of A monomers include acrylic acid, methacrylic acid, N,N-dimethylacrylamide, dimethyl aminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, methacrylamide, N-t-butyl acrylamide, maleic acid, maleic anhydride and its half esters, crotonic acid, itaconic acid, acrylamide, acrylate alcohols, hydroxyethyl methacrylate, diallyldimethyl ammonium chloride, vinyl pyrrolidone, vinyl ethers (such as methyl vinyl ether), maleimides, vinyl pyridine, vinyl imidazole, other polar vinyl heterocyclics, styrene sulfonate, allyl alcohol, vinyl alcohol (such as that produced by the hydrolysis of vinyl acetate after polymerization), vinyl caprolactam, salts of any acids and amines listed above, and mixtures thereof. Preferred A monomers include acrylic acid, N,N-

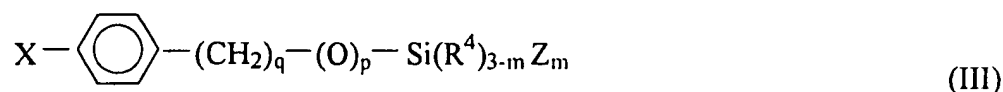
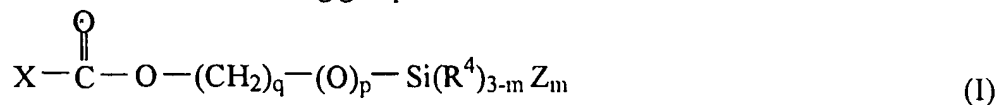
dimethyl acrylamide, dimethylaminoethyl methacrylate, quaternized dimethyl aminoethyl methacrylate, vinyl pyrrolidone, salts of acids and amines listed above, and mixtures thereof.

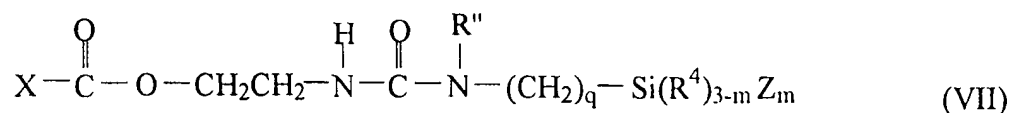
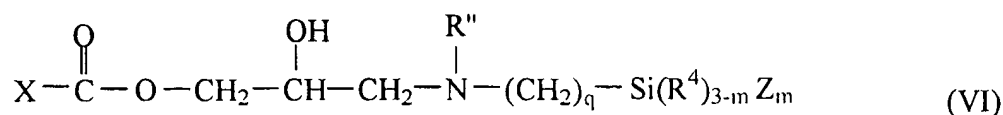
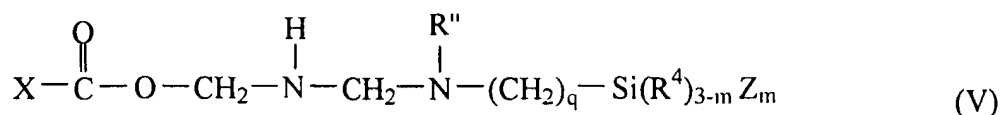
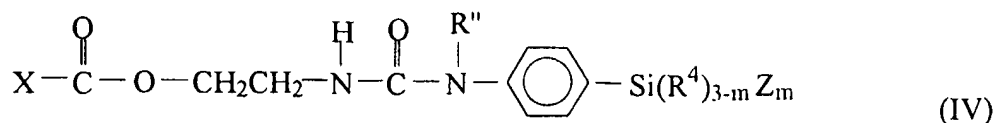
Representative examples of B monomers are acrylic or methacrylic acid esters of C₁-C₁₈ alcohols, such as methanol, ethanol, methoxy ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 1-methyl-1-butanol, 3-methyl-1-butanol, 1-methyl-1-pentanol, 2-methyl-1-pentanol, 3-methyl-1-pentanol, t-butanol(2-methyl-2-propanol), cyclohexanol, neodecanol, 2-ethyl-1-butanol, 3-heptanol, benzyl alcohol, 2-octanol, 6-methyl-1-heptanol, 2-ethyl-1-hexanol, 3,5-dimethyl-1-hexanol, 3,5,5-tri methyl-1-hexanol, 1-decanol, 1-dodecanol, 1-hexadecanol, 1-octa decanol, and the like, the alcohols having from about 1-18 carbon atoms with the number of carbon atoms preferably being from about 1-12; styrene; polystyrene macromer; vinyl acetate; vinyl chloride; vinylidene chloride; vinyl propionate; alpha-methylstyrene; t-butylstyrene; butadiene; cyclohexadiene; ethylene; propylene; vinyl toluene; and mixtures thereof. Preferred B monomers include n-butyl methacrylate, isobutyl methacrylate, t-butyl acrylate, t-butyl methacrylate, 2-ethylhexyl methacrylate, methyl methacrylate, and mixtures thereof. Most preferably, B is selected from t-butyl acrylate, t-butyl methacrylate, and mixtures thereof.

Polymerizable polysiloxane-containing monomers (C monomer) are exemplified by the general formula:



wherein X is an ethylenically unsaturated group copolymerizable with the A and B monomers, such as a vinyl group; Y is a divalent linking group; R is a hydrogen, hydroxyl, lower alkyl (e.g. C₁-C₄), aryl, alkaryl, alkoxy, or alkylamino; Z is a monovalent siloxane polymeric moiety having a number average molecular weight of at least about 500, is essentially unreactive under copolymerization conditions, and is pendant from the vinyl polymeric backbone described above; n is 0 or 1; and m is an integer from 1 to 3. C has a weight average molecular weight as described above. Preferably, the C monomer has a formula selected from the following group:

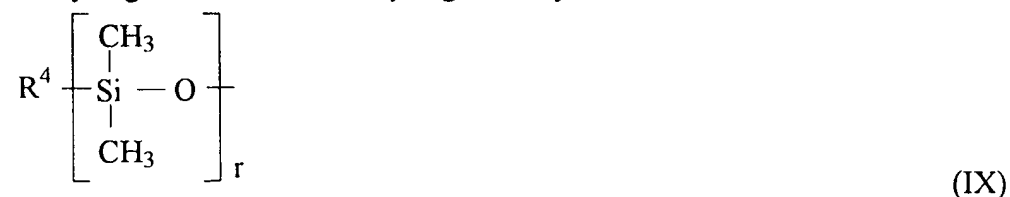




In those structures, m is 1, 2 or 3 (preferably m = 1); p is 0 or 1, preferably 0; R'' is alkyl or hydrogen; q, in all but (III), is an integer from 2 to 6; and q in (III) is an integer from 0 to 6; X is



R¹ is hydrogen or -COOH; R² is hydrogen, methyl or -CH₂COOH; Z is



R⁴ is alkyl, alkoxy, alkylamino, aryl, or hydroxyl (preferably R⁴ is alkyl); and r is an integer from about 5 to about 700.

In general, the silicone grafted polymer will preferably comprise from about 50% to about 99%, more preferably from about 60% to about 98%, most preferably from about 75% to about 95%, by weight of the polymer, of non-silicone macromer-containing monomer units, e.g. the total A and B monomer units, and from about 1% to about 50%, preferably from about 1% to about 40%, more preferably from about 2% to about 25%, of silicone macromer-containing monomer units, e.g. the C monomer units. The level of A monomer units can be from about 1% to about 99%, preferably from about 5% to about 80%, more preferably from about 10% to about 50%, most preferably from about 15% to about 40%; the level of B monomer units, can be from 0% to about 99%, preferably from about 1% to

about 90%, more preferably from about 5% to about 85%, most preferably from about 15% to about 80%; and the level of C monomer units, from about 1% to about 50%, preferably from about 1% to about 40%, more preferably from about 2% to about 25%.

The composition of any particular silicone grafted polymer will help determine its formulational properties. By appropriate selection and combination of particular A, B and C components, the silicone grafted polymer can be optimized for inclusion in specific vehicles. The backbone of the silicone grafted polymer included in the compositions hereof must be soluble in the polar solvent, which is hereinafter referred to as the silicone grafted polymer, as a whole, being soluble in the polar solvent. This is determined according to whether the polymer can stay in solution or precipitates out of solution at 25°C at the concentration present in the composition or whether the range of concentrations for silicone grafted polymer described herein. It is well within the skill of one in the art to select monomers for incorporation into the polymers for formulateability and solubility in selected polar solvent systems.

Exemplary silicone grafted polymers for use in the present invention include the following:

- (i) acrylic acid/n-butylmethacrylate/polydimethylsiloxane (PDMS) macromer
20,000 molecular weight macromer
- (ii) dimethylaminoethyl methacrylate/isobutyl methacrylate/2-
ethylhexyl-methacrylate/PDMS macromer-20,000 molecular weight macromer
- (iii) t-butylacrylate/acrylic acid/PDMS macromer-10,000 molecular weight
macromer
- (iv) t-butylacrylate/acrylic acid/PDMS macromer-20,000 molecular weight
macromer

Propellant

Aerosol hair spray and mousse product forms further comprise a propellant. When used, the propellant is used at levels from about 3% to about 15%, and preferably from about 5 to about 12% of the leave-on hair care composition. The propellant can comprise a hydrocarbon propellant selected from the group consisting of propane, n-butane, isobutane, n-pentane, isopentane, and hexane, and mixtures thereof or non-hydrocarbon propellants selected from the group consisting of carbon dioxide, nitrous oxide (especially N₂O), fluorohydrocarbons, fluoro-chlorohydrocarbons, and mixtures thereof, or mixtures of hydrocarbon and non-hydrocarbon propellants. A preferred propellant identified by the industry designation A-46 is a mixture of n-butane, isobutane, and propane in proportions chosen such that the blend has a vapor pressure of 46 psig at 70°F. Another preferred propellant for the present invention comprises 85% isopentane and 15% isobutane.

When no propellant is used, a non-aerosol composition may be provided in standard non-aerosol spray pumps or in a package equipped with an air or gas mixing device to achieve a non-aerosol foam.

Silicone Conditioning Agent

The hair care compositions of the present invention may also optionally include silicone conditioning agents, including nonvolatile soluble or insoluble silicone conditioning agents, or volatile silicone conditioning agents. However, the silicone hair conditioning agent must be used at very low levels. The silicone conditioning agents are used at levels less than about 1%, preferably less than 0.5%, and more preferably less than 0.25%, by weight of the hair care composition. It is most preferable that the hair care compositions of the present invention are essentially free of silicone conditioning agents. By essentially free it is meant is that there less than about 0.1% of the silicone conditioning agents in the leave-on hair care composition. Use of the silicone conditioning agents at levels higher than 1% could result in higher than desired deposition of the agent resulting in dirty, oily feel. Also, high levels of silicone deposition from a leave-on product would lead to build-up problems.

Silicone conditioning agents as well known in the art. References disclosing suitable silicone conditioning agents include U.S. Pat. No. 5,674,478, Dodd; U.S. Pat. No. 2,826,551, Geen; U.S. Pat. No. 3,964,500, Drakoff; U.S. Pat. No. 4,364,837, Pader; and U.S. Pat. No. 4,152,416, Spitzer et al. All of these patents are incorporated herein by reference.

Quaternary Conditioning Agent

The hair conditioning component of the hair care compositions of the present invention may also optionally include quaternary ammonium conditioning agents. However, the quaternary ammonium conditioning agent must be used in the leave-on hair care compositions of the present invention at very low levels. The quaternary ammonium conditioning agents are preferably used at levels less than about 2%, preferably less than 1.0%, and more preferably less than 0.5%, by weight of the hair care composition. It is preferable that the hair care compositions of the present invention are essentially free of the quaternary ammonium conditioning agents. Again, by essentially free it is meant that the composition contains less than about 0.1% of the quaternary ammonium conditioning agent. Leave-on compositions with higher levels of quaternary conditioners could deposit higher than desired levels of the agent resulting in dirty hair feel and build-up problems.

Quaternary ammonium conditioning agent which may be used include, but are not limited to, ester substituted quaternary ammonium compounds, such as monoester, diester and triester quaternary ammonium compounds; and amide substituted quaternary ammonium compounds, such as monoamide, diamide and triamide quaternary ammonium compounds. Quaternary ammonium conditioning agents also include dialkyldimethylammonium chlorides,

wherein the alkyl groups have from about 12 to about 22 carbon atoms and are derived from long-chain fatty acids, such as hydrogenated tallow fatty acid.

Hair Reducing Agents

The leave-on hair care compositions of the present invention are free of any hair reducing agents including thioglycolic acid, thioglycolic acid derivatives, cysteine, N-acylcysteines, salts of these compounds, thioglyceryl alkyl ethers, mercaptoalkylamides, sulfites and hydrogensulfites. Use of these hair reducing agents can potentially damage the hair and, in fact, make frizz more severe. The compositions of the present invention should contain less than 0.1%, and preferably less than 0.01% of these reducing agents.

METHODS OF MANUFACTURE

The leave-on hair conditioning compositions of the present invention are made via art recognized techniques for the various forms of personal cleansing products.

METHOD OF USE

The leave-on hair care compositions of the present invention are used in conventional ways to provide the frizz reduction benefits of the present invention. Such method of use depends upon the type of composition employed but generally involves application of a safe and effective amount of the product to the hair of a person in need of such treatment, combing or brushing the hair, and drying the hair or allowing the hair to dry. By "effective amount" is meant an amount sufficient enough to provide a hair conditioning benefit. In general, from about 1g to about 50g is applied to the hair on the scalp. The composition is distributed throughout the hair by, typically by rubbing or massaging the hair and scalp with ones' hands, by another's hands or using a comb or brush.

Preferably, the composition is applied to wet or damp hair prior to drying of the hair. After such compositions are applied to the hair, the hair is combed or brushed to achieve a styled in accordance with the desires of the user, and then dried. Alternately, the composition may be applied to dry hair, and the hair is then combed or styled in accordance with the desires of the user, and dried or allowed to dry.

EXAMPLES

The following examples illustrate the present invention. It will be appreciated that other modifications of the present invention within the skill of those in the hair care formulation art can be undertaken without departing from the spirit and scope of this invention.

All parts, percentages, and ratios herein are by weight unless otherwise specified. Some components are obtained from suppliers as dilute solutions. The levels given reflect the weight percent of the active material, unless otherwise specified.

Abil® B8851	0.00	0.00	0.00	0.00	0.00	0.00	2.50
Silicone Grafted Copolymer ¹	0.00	0.75	0.00	0.50	0.00	0.50	0.75
Preservative	0.35	0.35	0.35	0.35	0.35	0.35	0.35
Perfume	1.00	1.00	1.00	1.00	0.05	0.20	0.20
Ethanol	0.00	70.00	0.00	70.00	0.00	0.00	0.00
Panthenol	0.05	0.02	0.00	0.02	0.05	0.00	0.00
Water	<u>88.60</u>	<u>14.88</u>	<u>83.65</u>	<u>1.13</u>	<u>84.55</u>	<u>87.70</u>	<u>90.10</u>
	100.00	100.00	100.00	100.00	100.00	100.00	100.00

¹ - 60% t-butyl acrylate/20% acrylic acid/20% silicone macromer (weight average molecular weight of silicone macromer of about 10,000), having a weight average molecular weight of about 150,000.

These products are prepared by dissolving the diol in the water and/or ethanol and mixing for several minutes until all of the premix is dissolved. The remaining ingredients are then added. Perfume is added last. All ingredients are added under mixing conditions. The product can be packaged in conventional non-aerosol pump spray containers and compressed air pump spray aerosol containers.

These compositions provide useful leave-on hair care products, which provide frizz reduction benefits to hair.

Mousse

The following is a hair mousse composition representative of the present invention.

<u>Premix</u>	<u>Example No.</u>		
<u>Component (wt%)</u>	<u>14</u>	<u>15</u>	<u>16</u>
1, 2 Hexane diol	15.00	7.50	0.00
n-Butyl Glycerol Ether	0.00	0.00	10.00
Ethanol	16.13	16.13	16.13
Cocamine oxide	0.65	0.65	0.65
Cocamide DEA	0.32	0.32	0.32
C ₁₂ /C ₁₃ Polyethoxylate(3)	0.00	0.00	2.00
Silicone Grafted Copolymer ¹	0.50	0.00	0.75
Perfume	0.11	0.11	0.11
Water	<u>67.29</u>	<u>75.29</u>	<u>70.04</u>
Total Premix	100.00	100.00	100.00

Mousse

Premix	93.00	93.00	93.00
Isobutane Propellant	<u>7.00</u>	<u>7.00</u>	<u>7.00</u>
	100.00	100.00	100.00

¹ - 60% t-butyl acrylate/20% acrylic acid/20% silicone macromer (weight average molecular weight of silicone macromer of about 10,000), having a weight average molecular weight of about 150,000.

The compositions are made by blending all of the ingredients except isobutane at ambient temperature until well mixed. Aluminum aerosol cans are then filled with 93 parts of this batch, affixed with a valve which is crimped into position, and lastly pressure filled with 7 parts isobutane.

These compositions provide useful leave-on hair care products, which provide frizz reduction benefits to hair.

Aerosol Hair Spray

An aerosol hair spray composition of the present invention is prepared as follows:

<u>Premix</u>	<u>Example No.</u>
<u>Component (wt%)</u>	<u>17</u>
1, 2 Hexane diol	10.00
Polyethylene Glycol 4	0.50
Panthenol	0.15
Silicone Grafted Copolymer ¹	0.75
Ethanol	74.35
Perfume	1.00
Disodium EDTA	0.20
<u>Water</u>	<u>13.05</u>
Hair Spray Premix	100.00

Aerosol Hair Spray

Hair Spray Premix	79.00
Isobutane Propellant	15.00
Difluoroethane Propellant	<u>6.00</u>
	<u>100.00</u>

¹ - 60% t-butyl acrylate/20% acrylic acid/20% silicone macromer (weight average molecular weight of silicone macromer of about 10,000), having a weight average molecular weight of about 150,000.

All of the premix ingredients are mixed together at ambient temperature until the polymer is dissolved. The mixture is placed in an aerosol can which is then equipped with a conventional aerosol spray can valve which is vacuum crimped in place. The propellants are then filled through the valve and the can is equipped with a conventional aerosol spray can activator.

These compositions provide useful leave-on hair care products, which provide frizz reduction benefits to hair.

Gel

Hair treatment gel compositions of the present invention is prepared as follows:

<u>Component (wt%)</u>	<u>Example No.</u>
	<u>18</u>
1,2 Hexane diol	10.0
Carbomer 940	1.0
Triethanolamine	0.6
Isosteareth-20	0.5
Benzophenone-4	0.1
Polyquaternium-11	0.5
Silicone Grafted Copolymer ¹	0.75
Perfume	1.0
Preservative	0.1
Water	<u>85.45</u>
	<u>100.0</u>

¹ - 60% t-butyl acrylate/20% acrylic acid/20% silicone macromer (weight average molecular weight of silicone macromer of about 10,000), having a weight average molecular weight of about 150,000.

Lotion

An leave-on hair treatment lotion composition of the present invention is prepared as follows:

<u>Component (wt%)</u>	<u>Example No.</u>
	<u>19</u>
1, 2 Hexane diol	15.0
Xanthan Gum	1.0
Sodium Benzoate	0.25
Cocamidopropyl betaine	0.08
Magnesium sulfate Heptahydrate	3.00
Silicone Grafted Copolymer ¹	0.05
Perfume	0.05
Water	<u>80.57</u>
	<u>100.00</u>

¹ - 60% t-butyl acrylate/20% acrylic acid/20% silicone macromer (weight average molecular weight of silicone macromer of about 10,000), having a weight average molecular weight of about 150,000.

The composition is made by mixing the above components together in a conventional manner. This composition provides useful leave-on hair care products, which provide frizz reduction benefits to hair.

WHAT IS CLAIMED IS:

1. A leave-on hair care composition comprising:
 - (a) from about 3% to 30%, by weight, of a C₂-C₁₀-alkyl glyceryl ether; and
 - (b) from about 70% to about 97%, by weight, of a polar solvent selected from the group consisting of water, C₂-C₃ monohydric alkanols, and mixtures thereof.
2. A leave-on hair care composition comprising:
 - (a) from about 3% to 30%, by weight, of a 1,2 C₅-C₈-alkane diols; and
 - (b) from about 70% to about 97%, by weight, of a polar solvent selected from the group consisting of leave-on vehicle comprising a hair care ingredient selected from the group consisting of C₂-C₃ monohydric alkanols and mixtures of C₂-C₃ monohydric alkanols and water.
3. A leave-on hair care composition comprising:
 - (a) from about 3% to 30%, by weight, of a diol selected from the group consisting of 1,2 C₅-C₈-alkane diols, C₂-C₁₀-alkyl glyceryl ethers, and mixtures thereof;
 - (b) from about 70% to about 97%, by weight, of a polar solvent selected from the group consisting of water, C₂-C₃ monohydric alkanols, and mixtures thereof; and
 - (c) from about 0.015 to about 20%, by weight, of a hair care ingredient selected from the group comprising conditioning agents, anionic surfactants, nonionic surfactants, thickeners, polymers, perfumes, preservatives, pH adjusting agents, coloring agents, propellants, vitamins and derivatives thereof, vitamin penetration aids, hair spray spray modifiers, and mixtures thereof;wherein the hair care composition comprises less than about 0.1% of hair reducing agents.
4. A leave-on hair care composition according to claim 3 wherein the hair care ingredient comprises an anionic surfactant selected from the group consisting of alkyl and alkyl ether sulfates, sulfated monoglycerides, sulfonated olefins, alkyl aryl sulfonates, primary or secondary alkane sulfonates, alkyl sulfosuccinates, acyl taurates, acyl isethionates, alkyl glycerylether sulfonate, sulfonated methyl esters, sulfonated fatty acids, alkyl phosphates, acyl glutamates, acyl sarcosinates, alkyl sulfoacetates, acylated peptides, alkyl ether carboxylates, acyl lactylates, and anionic fluorosurfactants.
5. A leave-on hair care composition according to claim 4 wherein the hair care agent further comprises a nonionic surfactant selected from the group comprising silicone surfactants, block copolymers of ethylene oxide and propylene oxide, and mixtures thereof.

6. A leave-on hair care composition according to claim 5 wherein the hair care composition comprises less than about 2% quaternized ammonium conditioning agents.
7. A leave-on hair care composition according to Claim 6, which comprises less than about 1% silicone conditioning agent.
8. A leave-on hair care composition according to Claim 7, which comprises less than 0.1% of the quaternized ammonium conditioning agent.
9. A leave-on hair care composition according to Claim 8, which comprises less than 0.1% of silicone conditioning agent.
10. A leave-on hair care composition according to Claim 9, which further comprises from about 0.1% to about 5% of a silicone grafted copolymer.
11. A leave-on hair care composition according to Claim 3, wherein said diol is selected from the group consisting of 1,2 pentane diol, 1,2 hexane diol, 1,2 heptane diol, n-hexyl glyceryl ether, and mixtures thereof
12. A leave-on hair care composition according to Claim 11, wherein said diol is selected from the group consisting of 1,2 pentane diol, 1,2 hexane diol, 1,2 heptane diol, n-hexyl glyceryl ether, and mixtures thereof
13. A leave-on hair care composition according to Claim 12, wherein said diol is 1, 2 hexane diol.
14. A leave-on hair care composition according to Claim 12, wherein said diol is n-hexyl glyceryl ether.
15. A leave-on hair care composition according to Claim 1, wherein the leave-on hair care composition is of a product form selected from the group consisting of a gel, a tonic, a lotion, a mousse, and a spray.
16. A leave-on hair care composition according to Claim 12, wherein the leave-on hair care composition is of a product form selected from the group consisting of a gel, a tonic, a lotion, a mousse, and a spray.

17. A leave-on hair care composition according to Claim 3 wherein the product form is selected from the group comprising a tonic and a non-aerosol hair spray; and the hair care ingredient comprises:

from about 0.01% to about 4%, by weight of the composition, of a perfume; and
from about 0.001% to about 1%, by weight of the composition, of a preservative.

18. A leave-on hair care composition according to Claim 3 wherein the product form is selected from the group consisting of an aerosol hair spray and a mousse; and the hair care ingredient comprises:

from about 0.01% to about 4%, by weight of the composition, of a perfume;
from about 0.001% to about 1%, by weight of the composition, of a preservative; and
a propellant.

19. A leave-on hair care composition according to Claim 3 wherein the product form is selected from the group consisting of a gel and a lotion:

from about 0.01% to about 4%, by weight of the composition, of a perfume;
from about 0.001% to about 1%, by weight of the composition, of a preservative; and
a thickener.

20. A method for reducing frizzed hair comprising:

(a) application of a safe and effective amount of the composition of Claim 1 to hair in need of such treatment.

21. A method for reducing frizzed hair comprising:

(a) application of a safe and effective amount of the composition of Claim 2 to hair in need of such treatment.

22. A method for reducing frizzed hair comprising:

(a) application of a safe and effective amount of the composition of Claim 3 to hair in need of such treatment.

23. A method for reducing frizzed hair comprising:

(a) application of a safe and effective amount of the composition of Claim 12 to hair in need of such treatment.

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 A61K7/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 43 20 744 A (DRAGOCO GERBERDING & CO) 5 January 1995 (1995-01-05) page 2, line 26 - line 29; claims 1-4; table 1 ---	2,3,6-9, 11-13, 15,16, 20-23
Y	DE 42 34 744 A (WELLA) 21 April 1994 (1994-04-21) the whole document ---	1-23
Y	US 4 954 335 A (JANCHIPRAPONVEJ) 4 September 1990 (1990-09-04) column 15, line 19 - column 16, line 8; claims 1-35 --- -/--	1-23

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"Z" document member of the same patent family

Date of the actual completion of the international search

15 November 1999

Date of mailing of the international search report

24/11/1999

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 41 40 474 A (SCHÜLKE & MAYR) 17 June 1993 (1993-06-17) page 2, line 21 -page 3, line 12; claims 1-16 ---	1, 3, 4, 15-23
A	EP 0 168 574 A (KAO CORPORATION) 22 January 1986 (1986-01-22) the whole document ---	1-23
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